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㊻ Für die Beurteilung der Patentfähigkeit in Betracht gezogene Druckschriften:

NICHTS ERMITTELT

㊱ Verfahren zur Ermittlung von Gaslecks in Brennstoffzellen

㊲ Bei einem Verfahren zur Ermittlung von Gaslecks zwischen dem Anoden- und Kathodengasraum von PEM-Brennstoffzellen wird in den beiden Gasräumen ein unterschiedlicher Wasserstoffpartialdruck eingestellt und der zeitliche Verlauf der Zellspannung gemessen.

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Description

The invention relates to a method for determining gas leaks between the anode and cathode space of PEM fuel cells.

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PEM fuel cells (PEM = polymer electrolyte membrane) comprise two gas-permeable, porous, electrically conductive collectors on the anode side and on the cathode side of an ion-conducting polymer membrane, which serves as an electrolyte; further, between each of collector and the membrane there is arranged a finely divided

10 catalyst. Each side of the fuel cell is supplied with a fuel gas, in particular, with hydrogen or a hydrogen-containing gas, and with an oxidant, in particular, oxygen or an oxygen-containing gas, such as air. Hydrogen is oxidized at the anode, with protons being produced, which diffuse through the membrane to reach the oxygen side. At the cathode, the protons recombine with reduced oxygen to become water. On the basis of

15 leakages in the membrane /electrode unit, gas may pass from one gas space to the other, with a reaction between hydrogen and oxygen taking place at the catalyst (gas short).

Fuel cells are used in building up fuel cell batteries consisting of a plurality of cells which are electrically connected in series. As for the development and operation of

20 such batteries, diagnosing methods are necessary, by means of which it is possible to detect diffusion and leakage rates, for example, and to locate defective cells, with gas shorts having to be recognized at an early stage, in particular.

So far is has not been possible to locate a cell with a gas short, which is arranged

25 in a multi-cell battery, without dismantling the same or effecting detailed inspections. Otherwise, one would take the risk of destroying major parts of the cell or even several cells, which practically makes it impossible to identify the causes. Moreover, in previous leakage test procedures, which are based on pressure loss measurement, a dangerous gas short might remain unidentified, since the leakage losses do not

30 distinguish themselves sufficiently from diffusion losses of the entire battery, yet, locally, they may result in the battery catching fire.

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It is an object of the invention to provide a simple method for identifying gas leaks between the anode space and the cathode space of PEM fuel cells and batteries, and which does not require the battery to be dismantled, this being particularly desirable with respect to the intended wide spread application of fuel cell batteries and the maintenance and repair stations necessary to this end.

According to the invention, this is achieved by setting a different hydrogen partial pressure in both gas spaces and by measuring the variation in time of the cell voltage.

In the leakage test method according to the invention, with which it is possible to determine the gas through-put rates in the individual cells independently of each other, it takes less effort to locate cells with a gas short. Since, during inspection, no gases able to react with each other are present in the battery, uncontrolled destruction may be excluded. Thus, in particular, no secondary damage as a result of fires in the interior of the battery are possible. This method further allows for a significant saving of labor, since the battery does not have to be dismantled for locating a cell having a gas short. Furthermore, no measuring instruments as are used in fluid mechanics are necessary, so that the method may be performed in a highly reliably, simple and quick manner.

In the method in accordance with the invention, the cell voltage, i. e. the voltage between the two electrodes (in the anode and the cathode space, respectively), is measured. Accordingly, it is also possible to determine the voltage applied to single cell packages or even the whole battery. As for the application of gas, distinguishing between the anode and cathode space is not necessary in this method.

Advantageously, the inventive method is further developed in the following manner:

-   Setting a higher gas pressure in the gas space having the higher hydrogen partial pressure;

- Supplying hydrogen or a hydrogen-containing gas to one of the two gas spaces, in particular, to the anode space, and supplying an inert gas, in particular, nitrogen, to the other gas space;
- At first, flooding the two gas spaces with the respective gas, and subsequently interrupting the inert gas supply, then measuring of the voltage.

For the quantitative evaluation of the leakage inspections, a so-called partial pressure increase coefficient is defined. This coefficient comprises a characteristic quantity with respect to a single diffusion exchange between both gas spaces of a cell. If a leakage exists, this value is greatly increased. In detail, this results in the following:

If, on the two sides (gas space 1 and 2) of an electrochemical cell, there is a reactive gas under various partial pressures p_1 and p_2, respectively, the following voltage is applied to the two electrodes in accordance with the Nernst equation:

$$U = (RT/zF) \bullet \ln(p_1/p_2),$$

where:

U: cell voltage

R: gas constant (8.314 J/Kmol)

T: temperature (K)

z: electrochemical valence (= 2 eqv/mol for hydrogen)

F: Faraday's constant (96487 C/eqv)

p_1, p_2: reaction partial pressure

A precondition is that the gas at the two electrodes may be transformed electrochemically. As for hydrogen, this is the case, e.g., with platinum electrodes. If p_2 is known, the following is obtained by means of a simple voltage measurement

$$p_1 = p_2 \bullet \exp(-UzF/RT).$$

The reference quantity p_2 must be known, and its relative change during measurement should be as small as possible. The latter is the case, if the absolute value is as great as possible and if gas space 1 is continuously flooded with fresh gas. In particular, when the temperature is high, the gases should be wetted, which is to be considered on a calculational basis. The total pressures P_1 and P_2 existing in the gas spaces have no direct influence on the measured value U, if the other gases being present are electrochemically inert gases.

In order to examine the gas exchanging processes between the two gas spaces of a cell, the appropriate procedure is as follows. Gas space 1 is charged with preferably pure nitrogen or any other inert gas, such as argon and helium, by using a humidifier, if necessary. Gas space 2 is charged with hydrogen by using another humidifier, if necessary. Commensurate with the partial pressure differences, the two gases diffuse through the membrane and the electrodes to reach the opposite side, where they effect a change in the gas composition. Already when continuously flooding the gas space using only very small amounts of gas, the influence of nitrogen on reference side 2 becomes negligibly small. First, when the exit is open, gas space 1 is also thoroughly rinsed. If, then, the gas supply is abruptly interrupted, the hydrogen partial pressure p_1 starts rising, and voltage U is decreasing. The expected variation in time of p_1 may be described by the following equation: $(dp_1/dt) = a(p_2-p_1)$.

If no leak exists between the two gas spaces, then pressure increase coefficient a depends only on the hydrogen diffusion characteristics of the materials used and on the effective thickness of the gas space. For a cell having a specific design, a is thus a characteristic constant a_D. If a leak exists between the two gas spaces, the increase coefficient – depending on the total pressure difference $P_2 - P_1$ - is generally increased: $a = a_D + a_L$. Thus, it is possible to identify a leak as such, if, within the area of measuring accuracy, proportion a_L may be clearly distinguished from diffusion share a_D.

In order to make the proportion of the leak a_L as great as possible, the absolute pressures P_1 and P_2 should refer to different amounts, if possible. In this respect, a difference of approx. 1 bar is appropriate. Undamaged membranes withstand the load caused as a result thereof without any danger of getting damaged. However, during a
5   leakage test, it is desirable to identify any previously caused damage. It is also important for the pressure on the reaction side to be greater than on the inert gas side (P2 >P1). Moreover, the evaluation of results should be restricted to the initial phase of pressure increase.

10   From the variation in voltage determined using a small test cell, the partial pressure was calculated using the equation as indicated above. With an input pressure of $P_2 = 2.1$ bar, a value of 1.6 bar (partial pressure of water vapor at 80 °C: 0.5 bar) results for reference pressure p_2. During flooding with nitrogen, the cell voltage rose to more than 1 V. This is a result of nitrogen containing small traces of oxygen. In the initial
15   phase of the measurement process, the permeating hydrogen is used for reducing oxygen and for changing the charge of the electrode. Shortening the duration of this phase is possible by applying a short-term load. It is not until then that p_1 rises significantly. From the variation of the hydrogen partial pressure, value triplets p_1, (dp_1/dt), and a were calculated. With respect to a wide range, the increase coefficient results in a =
20   1.3 / h. In a second identical cell, a value of 1.2 / h was determined for a.

In a defective cell, i. e. in a cell having a gas leak, the calculated variation in partial pressure initially resulted in a pressure increase coefficient of approx. 17/h. As compared to a normal case, this value is thirteen-fold increased. The associated gassing
25   rate is approx. 1 l/h. A subsequently repeated measurement resulted in a value for the increase coefficient a of even 77 / h.

The measurements show that, by means of the inventive method, it is possible to determine a pressure increase coefficient having a characteristic quantity for a cell of a
30   certain design and a certain temperature. In a cell with a gas short, this value is considerably increased, especially when a corresponding total pressure difference is

effective between the two gas spaces during measurement. In this manner, defective cells in a combination of batteries may be located easily.

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Patent claims

1. Method for determining gas leaks between the anode and the cathode gas space of PEM fuel cells, **characterized in that,** in the two gas spaces, a different hydrogen partial pressure is set and that the variation in time of the cell voltage is measured.

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2. Method according to claim 1, characterized in that, in the gas space having the higher hydrogen partial pressure, a higher gas pressure is set.

3. Method according to claim 1 or 2, characterized in that the one gas space, in

15 particular, the anode gas space, is supplied with hydrogen or a hydrogen-containing gas, and that the other gas space is supplied with an inert gas, in particular, nitrogen.

4. Method according to claim 3, characterized in that the two gas spaces are at first flooded with the respective gases and that afterwards the inert gas supply is interrupted.

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